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HYDROGEN PERMEABILITY OF BOROSILICATE GLASSES

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Borosilicate glass-forming compositions $R_2O - B_2O_3 - SiO_2 - R_aO_b$ (R — Li, Na, K; R_a — Zn, PbO) are investigated. A correlation-regression analysis of the criteria (the silicate modulus, the oxygen number, the structure cohesion factor, the relative molar volumes of the components) affecting the hydrogen permeability of glasses is carried out. The tendency for permeability variations depending on the component composition and the above specified criteria is identified.

Glass microspheres used for making glass-reflecting coatings used in agriculture, construction, medicine, and in laser physics experiments as microballoons should have a low level of hydrogen permeability (hereafter "permeability"). However, there is yet no method for the development of compositions providing for this property.

The purpose of the present study was to analyze some criteria that influence the permeability of borosilicate glasses.

The properties of materials are determined by their structure; therefore, the permeability (estimated by the coefficient K [1]) depends on the material structure as well. The structure-determining criteria Kr of glasses include the silica modulus n_{Si} [2]. The composition of glass is related to the structure cohesion factor Y [3], which, as well as the silica modulus, determines the type of the lattice: tridimensional, laminar, chain, or insular. Boron (one of the glass-forming elements) can change its coordination with respect to oxygen and form tetrahedra or flat triangular structural units, incorporate into the silicon-oxygen lattice, or form its own structure. The content of boron in different coordination states is determined using the oxygen number O [4]. One criterion may be the relative molecular volume V_i of the oxide i in the glass lattice. The calculation formulas are given bellow:

$$n_{Si} = \frac{C_{SiO_2}}{C_{Na_2O}};$$

$$Y = \frac{\sum_j x C_j \, z - \sum_k x C_k}{\sum_j x C_j};$$

$$O = \frac{C_{PbO} + \sum C_{RO} + \sum C_{R_2O} - \sum C_{Al_2O_3}}{\sum C_{B_2O_3}};$$

$$V_i = \frac{m_i \overline{V}_i}{\sum_i m_i \overline{V}_i} \times 100;$$

$$K = 8.1 \times 10^{-14} \exp\left[-\frac{1}{T}(17{,}330 - 127.8G)\right],$$

where C is the molar content, %; x is the number of cations in the oxide; j are oxides containing cations with more than one bond; k are oxides containing cations with number of bonds equal to unity (R_2O); z is the valence of the respective metal; m_i is the molar part of the oxide; $\overline{V}_i$ is the partial molar volume of the oxide, cm^3/mole; T is the temperature, K; and G is the sum of the glass-formers in the borosilicate system ($C_{SiO_2} + C_{B_2O_3}$).

All compositions contained B_2O_3; therefore, we calculated the borosilicate modulus n_{BSi} and substituted the sum ($C_{SiO_2} + C_{B_2O_3}$) into the numerator of the first formula. Figure 1 shows the variations of the moduli (as there were no significant differences, n_{BSi} thereafter was not considered).

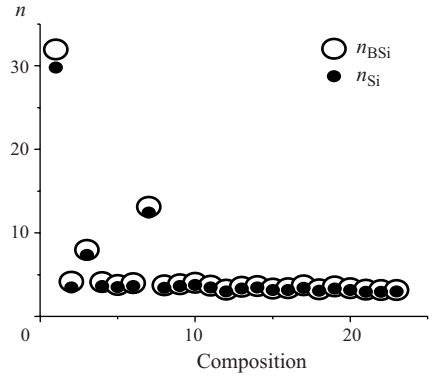

Fig. 1. Changes in the silica modulus n_{Si} and the borosilicate modulus n_{BSi}.

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The borosilicate system selected for the study was the one most commonly used in microsphere glass, in particular, the $R_2O - B_2O_3 - SiO_2 - R_aO_b$ (R — Li, Na, K; R_a — Zn, PbO) compositions. The structural criteria and the content of the components in the compositions for making microspheres are listed in Table 1. Compositions 1 – 4 and 7 were taken from the studies described in [5, 6] and the others were obtained by us in an aqueous medium using the sol-gel method. All components were split in three groups: glass-forming agents *gf* (SiO_2, B_2O_3), modifiers *mod* (Li_2O, Na_2O, K_2O), and additional oxides *ad* (ZnO, PbO). To determine the *Kr* that might affect the hydrogen permeability log *K*, a correlation-regression analysis was carried out, correlation coefficients *R* were calculated, and linear regression equations were constructed [7], including equations for the number *O* and the factor *Y* (while affecting the permeability, they themselves depend on the composition and ratio of the main oxides (SiO_2 and Na_2O). Table 2 lists only the results corresponding to $R \geq 0.5$.

The permeability in the considered compositions (Fig. 2, curve *3*) may increase with increasing content of the glass-formers, whereas the modifiers decrease the permeability (Fig. 2, curves *1* and *2*). The effect of the additional oxides is ambiguous, since the respective curve *4* is a parabola. An analysis of the components indicates that log *K* varies in proportion to V_{SiO_2} and is in inverse proportion to V_{Na_2O} (Fig. 2*c*, curve *6*). Tin, potassium, and boron oxides have an ambiguous effect on the permeability: the respective curves *5*, *7*, and *8* are parabolas. The role of K_2O depends on the fact that it is an alkali components and a "donor" of oxygen (the *O* number increases) to form [SiO_4] and [BO_4] tetrahedra, thus creating borosilicate patterns. As a consequence, the structure becomes more ordered.

As the positive charge accumulates at the expense of the cations R^+, stressed areas arise in the structure. As the stresses relax, part of the bridge bonds Si – O – Si are ruptured, the amorphous state of the lattice increases, and its cohesion decreases. This confirms the dependence of log *K* on n_{Si} and *Y*: the greater the V_{SiO_2}, the higher the probability of formation of high-modulus silicates and a more coherent lattice (n_{Si} and *Y* increase) approaching the structure of quartz glass. However, quartz glass is the most gas-permeable material [8].

The effect of B_2O_3 is accounted for as follows. The permeability grows when boron-oxygen tetrahedra emerge and are incorporated into the silicate skeleton. This is due to the *O* number growing due to R_2O oxides and is accompanied by an increase in the value of the factor *Y*. As the content of R_2O decreases, the *O* number decreases and, as a consequence of the emergence of some flat [BO_3] groups, conditions develop for boron to form its own structure. The character of the changes in curves *7* and *8* shows that K_2O (as distinct from Na_2O) has a direct effect on the coordination state of boron. The effect of Na_2O is undoubtedly significant: it is one of the main component both with respect to its content

TABLE 1

Composition	Criteria					Relative molar volume, %								
	log *K*	n_{Si}	n_{BSi}	*O*	*Y*	SiO_2	B_2O_3	Na_2O	K_2O	Li_2O	PbO	glass-formers	modifiers	additional oxides
1	– 23.00	29.80	31.96	31.63	3.65	83.38	1.75	0.88	4.34	–	–	87.55	12.45	–
2	– 23.63	3.46	4.15	4.13	3.30	73.35	10.28	16.37	–	–	–	83.63	16.37	–
3	– 23.72	7.36	7.99	7.84	3.47	78.43	4.68	8.13	8.76	–	–	83.11	16.89	–
4	– 23.96	3.63	4.11	4.06	3.34	82.40	7.57	9.17	–	–	1.33*	89.97	10.03	0.86
5	– 24.11	3.49	3.79	3.72	3.81	75.94	4.58	16.75	2.46	0.27	–	80.52	19.48	–
6	– 24.24	3.66	3.97	3.90	3.30	75.26	4.53	15.81	4.13	0.27	–	79.79	20.21	–
7	– 24.30	12.45	13.12	12.82	3.66	85.78	3.20	5.23	5.79	–	–	88.98	11.02	–
8	– 24.45	3.43	3.72	3.65	3.27	74.27	4.49	16.72	4.24	0.28	–	78.76	21.24	–
9	– 24.53	3.66	3.87	3.79	3.22	75.66	3.20	15.93	2.63	2.46	0.12	78.86	21.02	0.12
10	– 24.64	3.78	4.01	3.92	3.20	74.89	3.20	15.27	4.05	2.47	0.12	78.09	21.79	0.12
11	– 24.77	3.46	3.67	3.59	3.17	74.30	3.18	16.60	3.33	2.46	0.13	77.48	22.39	0.13
12	– 24.80	2.97	3.22	3.17	3.22	73.81	4.46	19.19	2.19	0.35	–	78.27	21.73	–
13	– 24.88	3.34	3.54	3.47	3.65	73.86	3.09	17.09	3.39	2.44	0.13	76.95	22.92	0.13
14	– 24.91	3.45	3.66	3.58	3.16	73.58	3.16	16.46	4.19	2.41	0.20	76.74	23.06	0.20
15	– 24.96	3.16	3.35	3.27	3.26	73.42	3.14	17.99	2.84	2.41	0.20	76.56	23.24	0.20
16	– 25.12	3.17	3.36	3.27	2.82	72.59	3.12	17.74	3.98	2.39	0.18	75.71	24.11	0.18
17	– 25.14	3.44	3.74	3.67	3.18	70.88	4.30	15.92	8.62	0.28	–	75.18	24.82	–
18	– 25.19	3.08	3.27	3.20	3.10	72.28	3.10	18.14	3.88	2.40	0.20	75.38	24.42	0.20
19	– 25.20	3.32	3.60	3.54	3.19	70.58	4.30	16.44	8.63	0.05	–	74.88	25.12	–
20	– 25.20	3.18	3.37	3.30	3.10	72.21	3.10	17.60	4.51	2.40	0.18	75.31	24.51	0.18
21	– 25.56	2.94	3.19	3.13	3.10	68.95	4.18	18.21	8.33	0.33	–	73.13	26.87	–
22	– 25.60	2.93	3.18	3.12	2.65	68.77	4.15	18.22	8.38	0.48	–	72.92	27.08	–
23	– 25.63	2.97	3.15	3.08	3.62	70.03	3.02	18.33	6.08	2.36	0.18	73.05	26.77	0.18

* Related to ZnO.

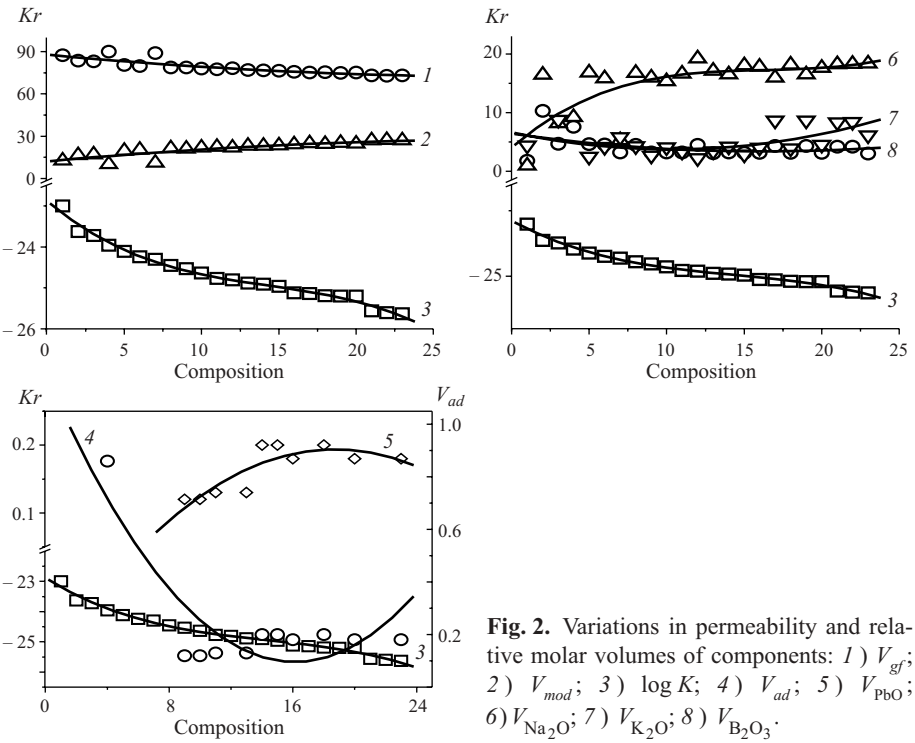

Fig. 2. Variations in permeability and relative molar volumes of components: *1*) V_{gf}; *2*) V_{mod}; *3*) log *K*; *4*) V_{ad}; *5*) V_{PbO}; *6*) V_{Na_2O}; *7*) V_{K_2O}; *8*) $V_{B_2O_3}$.

and its structure-forming role. However, its effect on the coordination state of boron is manifested after the silicon-oxygen lattice is formed. Phase separation in boron-containing compositions often occurs in the form of drop liquation, which was observed in gel drying; the composition of the drops had an increased boron content (Fig. 3).

Lead (same as boron) can form different coordination polyhedra [9], i.e., [PbO_8], [PbO_6], and [PbO_4]; however,

TABLE 2

Kr_1*	Kr_2*	*R*	Regression equation of the form of $Kr_1 = A + B\,Kr_2$	Kr_2 value			Kr_1 value		
				minimum	average	maximum	minimum	average	maximum
log *K*	V_{gf}	0.9	$-34.13 + 0.12V_{gf}$	72.92	81.44	89.97	– 25.38	– 24.36	– 23.33
	V_{mod}	– 0.9	$-22.11 - 0.12V_{mod}$	10.03	18.56	27.08	– 23.31	– 24.34	– 25.36
	V_{ad}	0.6	$-25.18 + 1.29V_{ad}$	0.12	0.49	0.86	– 25.02	– 24.55	– 24.07
	V_{SiO_2}	0.8	$-33.72 + 0.12V_{SiO_2}$	68.77	77.28	85.78	– 25.47	– 24.45	– 23.43
	$V_{B_2O_3}$	0.5	$-25.43 + 0.18V_{B_2O_3}$	3.02	6.65	10.28	– 24.89	– 24.23	– 23.58
	V_{Na_2O}	– 0.7	$-22.99 - 0.11V_{Na_2O}$	0.88	9.60	18.33	– 23.09	– 24.05	– 25.01
	V_{PbO}	– 0.7	$-23.99 - 6.07V_{PbO}$	0.12	0.16	0.20	– 24.72	– 24.96	– 25.20
	n_{Si}	0.6	$-25.04 + 0.07n_{Si}$	2.93	16.36	29.80	– 24.83	– 23.89	– 22.95
	O	0.6	$-25.06 + 0.07O$	3.08	17.36	31.63	– 24.84	– 23.84	– 22.85
	Y	0.5	$-29.09 + 1.35Y$	2.65	3.23	3.81	– 25.51	– 24.43	– 23.95
O	n_{Si}	1.0	$0.07 + 1.08n_{Si}$	2.93	16.36	29.80	3.23	17.74	32.25
	C_{K_2O}	0.6	$-1.45 + 1.80C_{K_2O}$	1.56	4.82	8.08	1.36	7.23	13.09
	C_{Na_2O}	– 0.9	$25.62 - 1.09C_{Na_2O}$	2.79	12.96	23.12	22.58	11.49	0.42
	C_{SiO_2}	0.8	$-62.17 + 0.97C_{SiO_2}$	64.70	75.98	87.26	0.59	11.53	22.47
Y	C_{Na_2O}	– 0.5	$3.76 - 0.03C_{Na_2O}$	2.79	12.96	23.12	3.68	3.37	3.07
	C_{SiO_2}	0.6	$1.16 + 0.03C_{SiO_2}$	64.70	75.98	87.26	3.10	3.44	3.78

* Kr_1 and Kr_2 are the criterion considered and the influencing criterion.

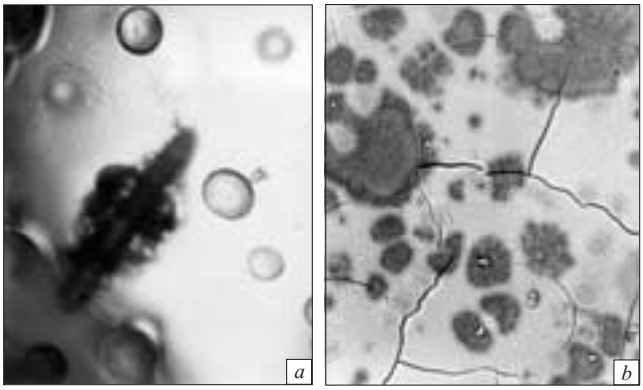

Fig. 3. Drop liquation in a gel of the $R_2O - B_2O_3 - SiO_2 - PbO$ composition: *a*) moist clear gel with a shadow image of the material migrating toward a growing lead silicate crystal (× 23); *b*) a dry material with fracture traces (× 200).

the considered compositions most probably did not contain lead-bearing tetrahedra capable of incorporating into the glass lattice. All lead, whose content and V_{Pb} are rather low (Table 1), could be localized in the structural cavities formed by broken bridge bonds. The effect of decreased permeability depends on its large size. The role of Li_2O and ZnO could not be interpreted due to lack of data, furthermore, the curve $\log K = f(V_{Li})$ had a weakly expressed parabolic shape.

Thus, the correlation-regression analysis helps to clarify the effect of the glass components on gas permeability and makes it possible to predict the trend of its variation. The high correlation coefficients confirm the expediency of using the silica modulus, the relative molar volume of the oxides, the oxygen number, and the structure cohesion factor as the criteria for studying the hydrogen permeability of borosilicate glasses.

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